

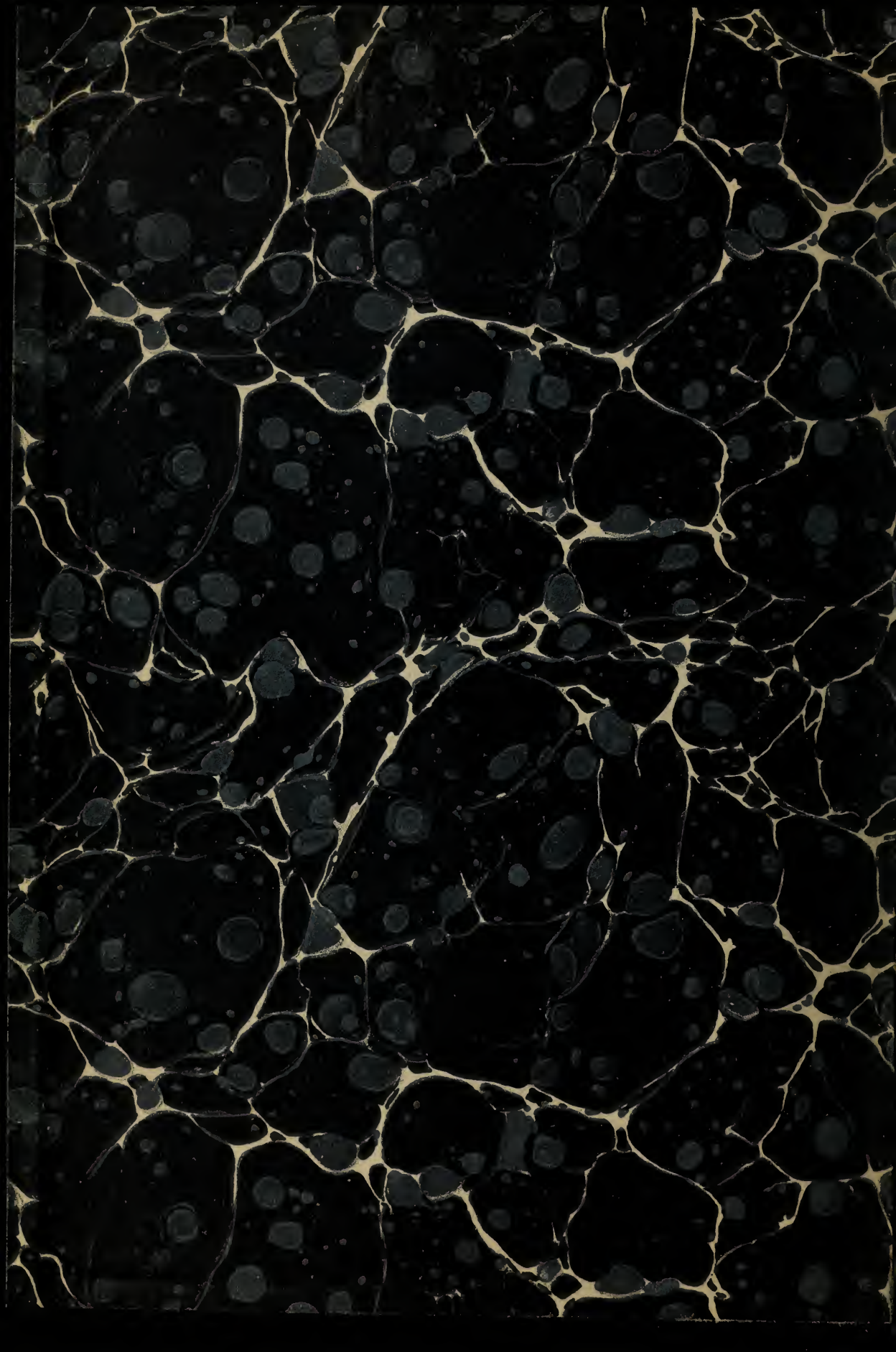
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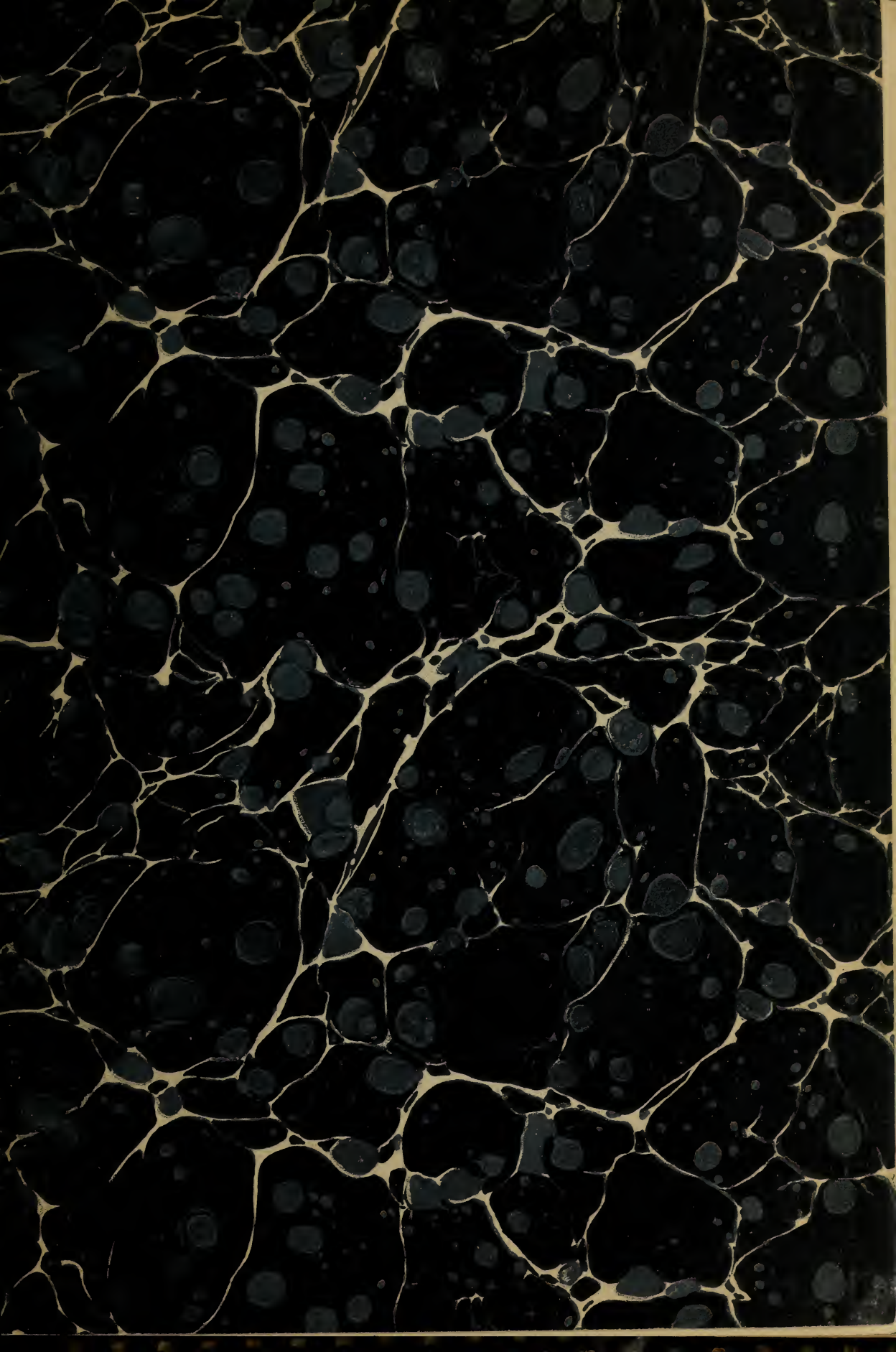
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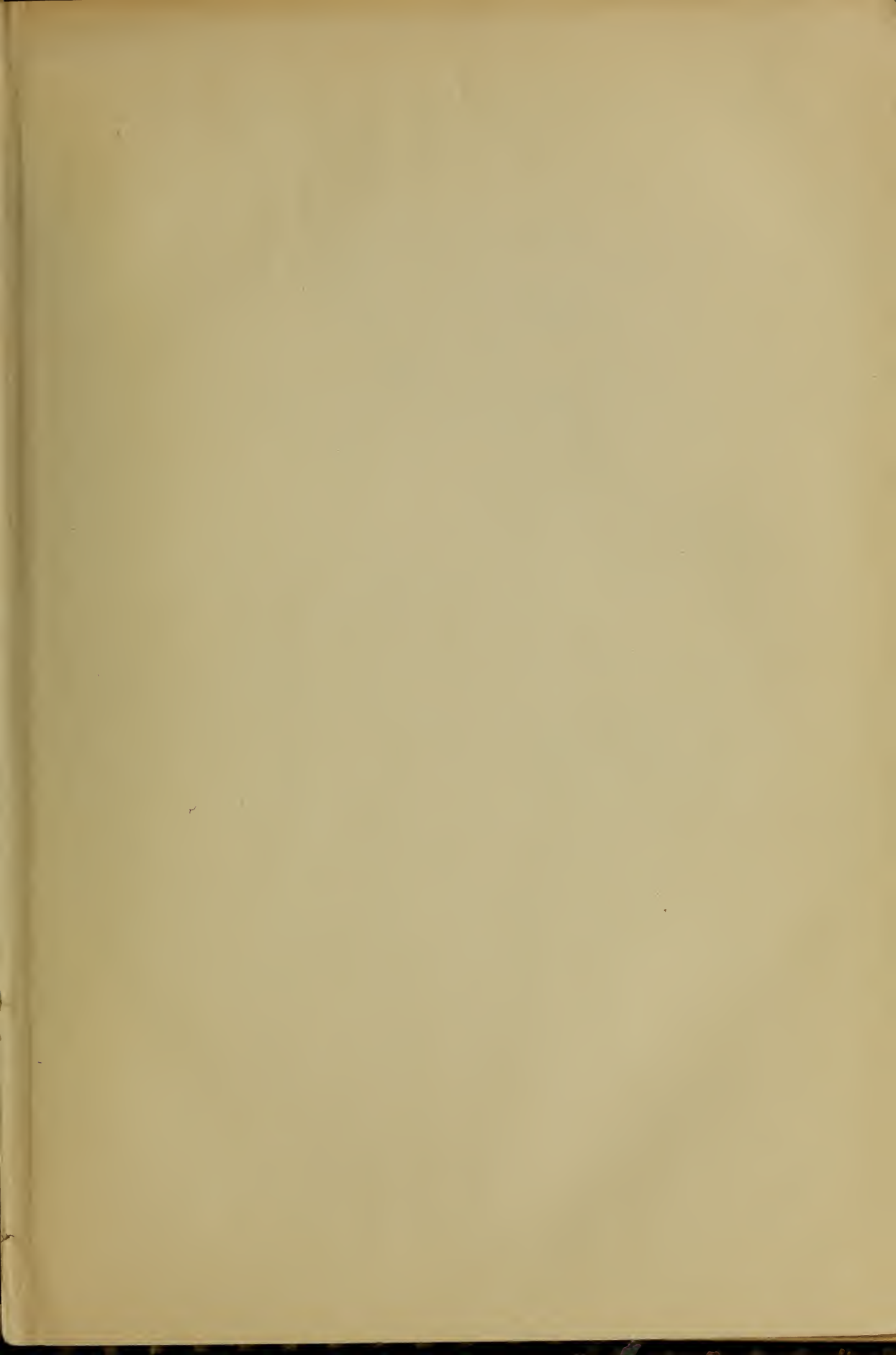
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DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 35

COMBUSTION METHOD FOR THE DIRECT
DETERMINATION OF RUBBER

BY

L. G. WESSON, Laboratory Assistant

Bureau of Standards

[FEBRUARY 13, 1914]



WASHINGTON
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COMBUSTION METHOD FOR THE DIRECT DETERMINATION OF RUBBER

By L. G. Wesson

The method most in use at the present time for the determination of the caoutchouc content of rubber goods is an indirect one, in which the sample is analyzed for its moisture, mineral matter, sulphur, resin, and other contents, these values being then added together and the sum subtracted from 100 per cent to arrive at the percentage of rubber present. As many of the best methods for estimating these constituents are admittedly inaccurate, the indirect method is not a satisfactory one. A number of direct methods have been proposed and thoroughly tested, but as they depend for their accuracy on certain derivatives of rubber, the nitrosite, the nitrosate, and the tetrabromide, that have not thus far been obtained with unvarying composition, these methods have not found general acceptance either as technical or research methods for this extremely important estimation. It is hoped that the method¹ about to be described will lend itself to development not only as a dependable one for rubber research work, but also for the commercial laboratory.

The procedure, in brief, consists first in forming the nitrosite of rubber by the action of nitrogen trioxide gas upon a finely ground and acetone-extracted sample of the rubber suspended in chloroform. After the completion of the action, the insoluble nitrosite, fillers, etc., are filtered from the chloroform, and the nitrosite is dissolved in acetone. The suspension of finely divided mineral matter is then allowed to settle out, or is thrown down with the centrifuge. An aliquot portion of the solution is transferred with a pipette to a small flask, and its volume reduced by evaporation

¹ A preliminary note on this method was published in the *Journal of Industrial and Engineering Chemistry*, 5, p. 398, 1913.

to a few cubic centimeters. This small volume of acetone solution of the nitrosite is now transferred with the help of ethyl acetate to a porcelain boat containing alundum, and, after the acetone and ethyl acetate have been expelled by warming the boat for several hours in a drying oven, the nitrosite is burned in a current of oxygen and the carbon dioxide thus formed is absorbed in soda-lime and weighed. If all of the carbon originally in the sample as rubber, and only such carbon, reaches the soda-lime apparatus as carbon dioxide through the intermediate nitrosite, the equation $C_{10}H_{16} = 10CO_2$ enables one to calculate the $C_{10}H_{16}$ or real caoutchouc content of the sample.

PROCEDURE AND APPARATUS IN DETAIL

The procedure and apparatus employed in obtaining the results given later are the outgrowth of many trials and experiments. Doubtless deviations are allowable in many points, but there was not opportunity to study the effect of changing various factors.

The sample should be ground to pass a 20-mesh sieve if possible, or cut up fine with the scissors if very soft. A weighed amount of the sample, 0.5 g for compounds containing about 50 per cent or less of rubber and 0.25 g for those containing a higher percentage, is wrapped into a bundle with a 9-cm filter paper and extracted for three to four hours with acetone in an apparatus of the Wiley or Cottle type, in which the sample is extracted by the solvent at the boiling point of the latter. The residue, from which the excess of acetone has been squeezed with the fingers, is then transferred to a 50-cc calibrated, glass-stoppered flask and allowed to dissolve or swell up in about 40 cc of chloroform,² which action may be hastened by warming the flask.

The rubber is now submitted to the action of nitrogen trioxide gas, evolved by running nitric acid of specific gravity 1.3 dropwise on arsenic trioxide contained in a flask warmed in a boiling water bath. After the gases have been passed through an empty gas-washing bottle to condense most of the moisture and nitric acid carried over from the generator, they enter the chloroform through a delivery tube joined by a rubber connection to the gas-

² The chloroform should not be previously dried, as moisture is apparently advantageous in giving a more rapid action of the nitrogen oxides on the rubber.

washing bottle and fitting closely end for end to the same. The flask containing the chloroform should be immersed in a beaker of cold water during the reaction, since the solubility of the oxides of nitrogen in chloroform is increased and the danger of the gas exerting a partial oxidation of the rubber to CO_2 is probably diminished thereby. The gas should be passed into the chloroform until a deep green color is obtained which is permanent for at least 15 to 20 minutes after the delivery tube has been disconnected from the gas generator.

The next morning the chloroform is decanted off, using gentle suction, through a small Gooch crucible provided with a mat of dry asbestos. If the filtrate is colored brown from the dissolved gases, one can be certain that a sufficient excess of the nitrogen oxide has been used. After the flask has been rinsed out several times with small volumes (5 cc) of chloroform, each time decanting carefully through the crucible, the excess of chloroform and acid vapors which remain in the flask should be expelled by the passage for a few minutes of a gentle air current through the original delivery tube. If some nitrosite from the rubber connection is on the upper end of this tube, it may be easily removed by moistening it with acetone and wiping clean with a piece of filter paper.

The nitrosite in the crucible is then dissolved by placing the crucible in a 75-cc beaker, adding successive small portions of acetone, and pouring each into the original flask until about 40 cc has been used. No harm is done if a portion of the asbestos gets into the flask. In the meantime, the delivery tube has been freed from the nitrosite by sucking some of the acetone up into it from the beaker and rinsing the outside into the same. Let the flask now remain in a beaker of water with occasional shaking, without stoppering, for a half hour to insure complete solution of the nitrosite in the acetone. The volume is now made exactly to the mark, the flask stoppered and shaken, and to obtain a clear solution the insoluble mineral matter is allowed to settle, or better, is quickly centrifuged out; 1500 revolutions per minute is sufficient to give a clear solution in from 5 to 10 minutes.

To regain the original temperature the flask is now allowed to stand again in the beaker of water until the correct volume is once more attained. An aliquot portion of the solution (25 cc) is now

pipetted to a 50-cc Erlenmeyer flask. To reduce the bulk of this solution to a few cubic centimeters the flask is warmed in a dish of water while a current of air is blown into the flask. The acetone should not be completely expelled. The nitrosite is transferred from the Erlenmeyer flask to a porcelain boat 14 cm long by 1.1 cm wide, and about two-thirds full of alundum,³ which is used to secure an even combustion of the nitrosite. The acetone solution of the nitrosite should not be poured into the boat, but should be drawn up into a small (2-cc) pipette and run out evenly over the alundum. Several 2 to 3 cc portions of ethyl acetate⁴ are then used to rinse out the remainder of the nitrosite, using a small wash bottle and the pipette for this purpose. Ethyl acetate is used for the expulsion from the nitrosite of acetone which is otherwise retained in small amounts, perhaps mechanically by the nitrosite or by the portion of the mineral matter which passes in solution with the nitrosite into the boat, or by reaction with the nitrosite during drying. When enough wash liquid has been added to the boat to show above the alundum, the most of it should be expelled by placing the boat for a few minutes in the drying oven. The same procedure should be repeated at least once, using small portions of ethyl acetate in the transfer as described above. When one is certain that no nitrosite remains in the flask or pipette, the boat is dried for two hours at about 85° C. A circulation of air in the oven to carry away the acetone and ethyl acetate vapors will assist the drying greatly. The nitrosite is now ready for the combustion.

The combustion apparatus as it was finally developed contains features already used outside of this laboratory,⁵ and others original either with my colleagues or myself. The arrangement of the parts is best understood from the figure.

The tube is of Jena combustion glass, or better, of quartz, 50 cm long and 1.5 cm bore. The nitrosite is decomposed by the heat of an external coil, made by winding two layers of nichrome

³ "RR" alundum, 90-mesh, specially prepared for carbon determinations. Norton Co., Worcester, Mass. A fresh portion should be used for each combustion.

⁴ The so-called "absolute ethyl acetate," containing about 2 per cent of alcohol. It should be redistilled before use, since it may contain other organic substances not easy to volatilize.

⁵ The most important of these are the electrically heated platinum coil used as a catalyzer (Morse and Taylor, *Am. Chem. J.*, **33**, p. 591, 1905); and the electrically heated external coil used for the decomposition of the substance to be burned.

ribbon,⁶ leaving 0.1 cm between the turns, on an asbestos-covered copper or brass tube, 5 cm long and of such a diameter as to leave a 0.3-cm space between the metal and the combustion tube; and then covering it with asbestos paper to form an insulating layer 1 cm thick. During the combustion the coil as it moves forward should never be moved so fast that its forward end reaches more than 1 cm beyond the border between the black carbon of the undecomposed nitrosite and the white alundum of the completely burned portion. The decomposition products are carried forward by the current of oxygen over a red-hot spiral of platinum wire, which serves as the catalyzer for complete oxidation. The spiral is made from 1.3 m of No. 20 wire wound into a cylinder 0.7 cm in diameter, and is supported in the middle of the tube by an unglazed porcelain or clay stem 12 cm long and 0.3 cm in diameter, the return end of the spiral passing back through the stem. The leads for the spiral are 8 cm long and are made with No. 10 platinum wire. One end of the pipestem is supported by these leads and the other end by a small leg of platinum wire. The leads may connect with the outside in one of several ways. There may be a rubber stopper at the forward end of the tube through which are pushed two heavy copper, nickel, or platinum wires, the ends of which are bent into small loops into which the platinum leads are placed before the insertion of the stopper. Nickel is the better of the first two metals named. The platinum wires are good, as they may be sealed into small glass tubes which reach just through the stopper. In any case the stopper soon deteriorates, although this action has no noticeable effect on the results of the combustion. The most satisfactory method, however, consists in drawing down the forward end of the combustion tube as in the diagram, joining on a 3-cm tube of 0.5-cm bore, and sealing in two 3-cm lengths of heavy platinum wire. These are bent up on the inside and the platinum leads are thrust forward so as to rest upon them.

The oxides of nitrogen formed during the combustion of the nitrosite are absorbed by a saturated solution of potassium bichromate in concentrated sulphuric acid. Acid vapors and sulphur trioxide are held back by 30-mesh granulated zinc. Attention is

⁶ 0.11×1/32", R=1.3 to 1.5 ohms per foot. Driver Harris Wire Co., Harrison, N. J.

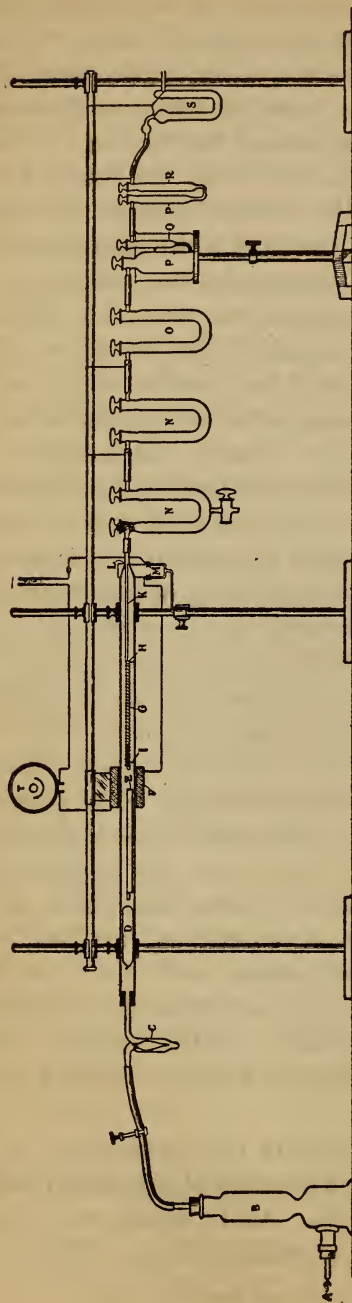


Fig. 1.—Form of apparatus for combustion of nitrosite and absorption of carbon dioxide

- | | |
|---|---|
| A. Oxygen enters. | L. Short platinum wires sealed into tube. |
| B. Moist soda lime. | M. Mercury contacts. |
| C. Bubble counter containing sulphuric acid (Dennstedt). | N, N. U tube containing glass beads and H_2SO_4 -
$K_2Cr_2O_7$. |
| D. Closed tube of Jena combustion glass, 8 cm long, to
prevent diffusion backward. | O. U tube containing 30-mesh granulated zinc. |
| E. Porcelain boat. | P, P. Soda lime. |
| F. Heating coil of nichrome ribbon. | Q. Calcium chloride. |
| G. Platinum spiral, about 10 cm long, of No. 20 wire. | R. Alumina. |
| H. Porcelain stem. | S. U tube containing palladium chloride solution. |
| I. Platinum leg for supporting stem. | T. Rheostat. |
| K. Platinum leads, 8 cm long, of No. 10 wire. | |

called to the form of apparatus in the figure for the absorption of carbon dioxide by soda lime. The capillary tube makes a good substitute for a stopcock on account of its comparative lightness, and is effective in separating the moist soda lime from the calcium chloride. Empty, the apparatus weighs 20 to 25 g and will hold 35 g of soda lime ⁷ and 7 g of calcium chloride. It will absorb 10 g or more of carbon dioxide without renewal. The second soda-lime tube contains alumina ⁸ in its second arm, which, it is thought, dries the gas to a degree comparable, for the purposes of the present work, to the drying by the concentrated sulphuric acid which precedes the soda-lime apparatus. To be certain that complete combustion is obtained, the gas finally passes through a faintly yellow solution of palladium chloride in water. While using the apparatus in its present form it has not been necessary to renew the palladium chloride solution, no sign of reduction having appeared in a number of combustions. The sulphuric acid-bichromate solution must be renewed in the first U-tube after every two or three analyses, while the zinc will last for a larger number of determinations.

CALCULATION

If 0.5 g sample, and 25 cc out of 50 cc of the acetone solution have been taken, the weight of CO₂ found multiplied by $\frac{136}{440} \times 4 \times 100 = 123.6$ gives the percentage of C₁₀H₁₆ on the basis of C₁₀H₁₆ = 10CO₂.

TIME REQUIREMENTS

For a single nitration about 15 minutes per sample is necessary; for the combustion, 30 to 45 minutes. Analyses of samples ground up in the forenoon of one day are completed the next. With one combustion tube two analyses may be run per day along with other work, while by using two tubes it is thought that, after some proficiency has been acquired, as many as four determinations can be made per day.

⁷ The J. T. Baker Chemical Co. furnishes a 12-mesh soda lime containing 15 per cent water, prepared for carbon dioxide absorption.

⁸ F. M. C. Johnson, J. Am. Chem. Soc., 34, p. 911, 1912.

FORMATION OF CARBON DIOXIDE FROM THE RUBBER DURING NITRATION

It is claimed by Alexander⁹ that during the formation of the nitrosite and nitrosate of rubber large quantities of carbon dioxide are evolved from the oxidation of the rubber by the nitrogen oxides. Gottlob,¹⁰ on the other hand, found only very small amounts of carbon dioxide. The writer made several tests of this important point by passing the gases from the rubber solution into a large volume of clear, saturated baryta water. Fine Para rubber, previously extracted with acetone and dried, was used for the experiments. After the chloroform, cooled as in the analytical procedure, had attained the deep green color, the apparatus was allowed to stand three to four hours, after which a current of carbon dioxide-free air was used to sweep into the barium hydroxide solution any carbon dioxide which might have formed during the interval. Only a trace of barium carbonate, a slight ring in the delivery tube, was formed, although the barium hydroxide solution remained alkaline throughout the experiment.

DETERMINATION OF THE SULPHUR OF VULCANIZATION

If the statement of Alexander¹¹ proves to be true that the sulphur of vulcanization of the rubber remains quantitatively in the nitrosite, this method could possibly admit of the simultaneous determination of the sulphur of vulcanization. An aliquot portion of the clear acetone solution of the nitrosite would be evaporated to dryness and the sulphur determined in the usual way.

RESULTS

The following results were obtained by the method above described. All are given that have been obtained on good quality, soft-vulcanized compounds since the date after which no great changes in the procedure were made. Whether the method is applicable to compounds of poor quality has not been determined, and as the author is no longer in a position to work on this point

⁹ *Zs. angew. Chem.*, **20**, p. 1358, 1907; **24**, p. 684, 1911.

¹⁰ *Ibid.*, **20**, p. 2213, 1907.

¹¹ *Ibid.*, **20**, p. 1364, 1907; **24**, p. 687, 1911; *Ber.*, **40**, p. 1077, 1907.

the field must be left to others. This Bureau may be able, however, to work in this field at some later date.

- A. A washed and dried up-river fine gave 94.0, 95.1, 95.8, and 95.9 per cent $C_{10}H_{16}$. Avg.=95.2 per cent plus 3.3 per cent acetone extr.=98.5 per cent.
- B. A commercial compound containing 45 per cent fine Para gave 42.0, 42.2, 42.7, 43.1, 43.3, and 43.4 per cent $C_{10}H_{16}$. Avg.=42.8 per cent plus 1.3 per cent acetone extr.=44.1 per cent.
- C. A commercial compound containing 48 per cent fine Para gave 44.8, 45.1, 45.1, and 45.3 per cent $C_{10}H_{16}$. Avg.=45.1 per cent plus 2.4 per cent acetone extr.=47.5 per cent.
- D. The same compound after standing finely ground for a month gave 43.4, 43.5, 43.5, and 45.0 per cent $C_{10}H_{16}$. Avg.=43.7 per cent.
- E. A commercial compound containing 25 per cent fine Para and 20 per cent caucho or 45 per cent gum gave 40.3, 40.4, 40.6, and 41.1 per cent $C_{10}H_{16}$. Avg.=40.6 per cent plus 3.2 per cent acetone extr.=43.8 per cent.
- F. A commercial compound containing 41.5 per cent coarse Para gave 39.5, 39.6, 39.8, and 40.1 per cent $C_{10}H_{16}$. Avg.=39.8 per cent plus 2.1 per cent acetone extr.=41.9 per cent.

SUMMARY

A new method for the direct determination of rubber is described, which is based upon the combustion of the nitrosite of rubber in a current of oxygen and weighing of the carbon dioxide thus formed. The results indicate a fair degree of reliability for both raw rubber and high-grade vulcanized compounds. The use of this method for the analysis of low-grade compounds and for the simultaneous determination of sulphur of vulcanization may be possible if its application to these fields is further studied.

During this work many valuable suggestions were made by Dr. W. F. Hillebrand, Mr. J. B. Tuttle, and a number of others at this Bureau, and I take this opportunity to express to them my appreciation of the same.

WASHINGTON, February 13, 1914.



